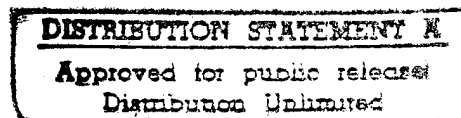




FIRST QUARTERLY STTR PROGRESS REPORT
OFFICE OF NAVAL RESEARCH CONTRACT N00014-95-C-0079

"A New Diamond Emitter Device"

April 10, 1995



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19951012 073

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FIGURES

1. Four zone Thermco belt furnace
2. Pitt vacuum furnace, 1600 C, H₂/N₂
3. Camco vacuum furnace, 1200 C, Air
4. Astro vacuum furnace, 1600 C, H₂/N₂
5. Raman equipment at NCSU
6. High vacuum 6 cross emission test chamber
7. UPS (ultraviolet photo-emission spectrometer)
8. Cu-C phase diagram a and b.
9. Raman spectra of samples
10. Sem photos of samples
11. Tektronix 576 curve tracer

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Introduction

First quarter contract effort involved the assembly of an infrastructure to conduct research and provide for the potential manufacture of metalized diamond devices. The following equipment was set up and used to produce and test some initial diamond emitter devices:

A Thermco 4 zone belt furnace (fig 1) capable of 1200 C with N₂ and H₂ gas flows was obtained for the STTR and set up. This furnace has N₂ curtains to allow for continuous production in inert or H₂ gas. This furnace may be used to bond diamond directly to a conductor in a high speed manufacturing process.

Three batch type vacuum ovens are operational and available through the PTS consultants:

A small 1600C Pit furnace (fig 2) made by Camco and plumed for both wet and dry N₂, H₂ or combinations.

A large vacuum bell furnace made by Camco, capable of 1200C (fig 3).

A larger vertical firing furnace made by Astro and capable of 1600C with N₂, H₂ or combinations (fig 4).

An 1100C pusher furnace made by Watkins Johnson was used to bond the initial diamond samples directly to copper using the Copper/Copper Oxide eutectic at ~1100C.

NCSU personnel (Mike Netzer et al) have examined initial samples using NCSU's scanning electron microscope and its' RAMAN spectrometer (fig.5).

A high vacuum (10E-8 torr) 6 cross vacuum chamber has been assembled at NCSU and instrumented to conduct NEA emission experiments (fig.6).

Several vials of single crystal, High Temperature-High Pressure (HT/HP)- synthetic Diamond grit samples from GE and others are available for this program. These samples are doped with Boron and Nitrogen. Grits normally used for superabrasives are also on hand. These low cost abrasive grits are used to set up equipment and test bonding and measurement apparatus.

A UPS (Ultraviolet photo-emission spectrometer) is operational (fig. 7) at NCSU and available for NEA evaluation of the existing metalized diamond emitter samples. The UPS equipment will be used to examine the potential NEA properties of existing samples during the months of April 95 and beyond.

Background

GE, the supplier of our current diamond samples, has operated the core diamond business in Worthington OH since the 1950's. GE supplies heavily contaminated (low resistivity) HP/HT diamond to the super abrasive industry. GE has conducted studies to make "iso-pure", or C12 diamond with near perfect transparency (70%) but at selling prices approaching \$10K per carat. GE also manufactures CVD polycrystalline, pure diamond at a cost of about \$110 for 5mm disks, (\$3200 for 25mm disks), 250 micrometers thick for heat sink and optical applications. GE has also developed proprietary metalization designs for sheet CVD diamond that involve a first layer of carbide forming metal, a second diffusion barrier layer of Pt metal and a third layer of Au. PTS may adopt some of these techniques by signing a non-disclosure agreement with GE.

PTS has purchased a new 1995 book entitled "DIAMOND: ELECTRONIC PROPERTIES AND APPLICATIONS" Edited by L.S. Pan and D.R. Kania and published by Kluwer. Sections 8 and 9 of this book give several processes to make good ohmic contacts to diamond. Also, section 10.3.1 indicate many attempts to create p-N heterojunctions which may prove useful for phase II of this work. Section 10.3.5 outlines techniques for creating NEA Emitters and sites a technique by M. Geis to implant carbon in p diamond to create a p-N like electron emitter with NEA. Section 10.4 also describes an electron beam activated switch where the electron beam modulates the conductivity of a high voltage diamond insulator at rf frequencies to produce a microwave amplifier.

The Research Triangle Park of NC is home to much of the research associated with electronic diamond materials and PTS has networked with many of the participants such as Kobe, Cree, NCSU, RTI, and a new company named Pendulum Electrodynamics (or Pental for short). The PTS consultants, Mr. Carl Everleigh and John Gathis are the principals of Pental. Pental has agreed to provide space for the tunnel oven equipment used in the metalizing experiments and has provided use of the vacuum ovens. PTS has also participated in a Semiconductor-Insulator-Semiconductor SBIR with BMDO and is familiar with some aspects of BMDO's Diamond Initiative. PTS also intends to network with ONR, BMDO, NRL, Sandia, Lawrence Labs, and NASA.

PTS is also working with Champion Aviation Products of Liberty SC, a division of Cooper Industries, to be a sponsor of the Phase III STTR effort. The specific Champion application is a high temperature switch for jet engine exciter/igniter applications.

Bonding and Contact Experiments

Several samples of random oriented single crystal diamond particles (crystallites) were bonded to preoxidized OFHC copper sheet in an inert (N₂) atmosphere at temperatures between 1065 and 1100 C. Mixed results were obtained, depending on temperature

accuracy, time, materials and conditions. When temperatures approached the melting point of copper and above, bonding was obtained; however, below 1083 C poor bonding resulted. It is believed that carbon gettered the oxygen that is needed for the copper-copper oxide direct bond process, but above 1085 C direct carbon to copper bonds were obtained. Apparently, some bonding is obtained above the Cu-C peritectic (1084.87C) point (fig. 8). Raman spectra of these direct bonded and possibly oxidized samples are poor and have been included in fig 9. SEM photographs of these abrasive grit, bonded samples are included in fig. 10. Improvements are expected when the clean, single crystal, doped GE samples are bonded to Cobalt/Nickel/Iron and/or to Ti substrates in a Hydrogen ambient gas.

A thick film paste consisting of diamond, copper and copper oxide powders was also formulated where the diamond comprised 20, 40, 60 and 80% of the composition (by weight). As a third bonding attempt diamond particles were pressed into copper at room temperature in an attempt to cold weld. These pressed samples were also fired at greater than 1000 C. In general, experiments that depended on the delicate copper-copper oxide balance failed. However, the thick film and cold weld Cu-C experiments hold promise.

Summary

The goal of the program is to produce and evaluate more efficient emitters using diamond semiconductor technology; and to propose use of electronic diamond technology in a phase II EBS (Electron Beam Semiconductor) device application. Accordingly, several samples of the rugged, type 6H SiC, high voltage EBS diode targets were obtained from Cree research. The SiC p-n junction diodes (20X20 mils) were evaluated on the PTS tektronix 576 curve tracer (fig. 11) and deemed suitable for use as reverse biased targets for the potential Phase II EBS device. These SiC devices have the potential to be more suitable as EBS targets than the Si diodes previously used. However, the small size will require paralleling until Cree can develop larger, defect free SiC crystals.

The first quarter progress involved:

Construction/Organization of a infrastructure to develop and manufacture diamond crystallite emitter devices.

An array of single crystal diamond crystallites samples, with various B and N dopings is available.

Preliminary samples of single crystal diamond crystallites bonded to copper have been produced.

Preliminary measurements involving SEM and RAMAN signatures of the copper diamond samples have commenced and are reported herein.

The first quarter activities culminated with RAMAN measurements of the bonded diamond crystallites. Figure 9 and figure 10 depict RAMAN and SEM results respectively. The RAMAN spectrum shows a weak diamond peak at 1336. The initial crystallites, normally used for superabrasives, may have been heavily oxidized and appeared to have a rough surface. Better samples were produced from the GE, HT/HP crystallites by pressing, or cold welding the crystallites to copper and firing at >1000 C. These samples are currently on hand.

A new metal substrate of cobalt nickel and iron is on hand. Bonding at >1450 C in a reducing hydrogen atmosphere is planned for the next reporting period. We also plan to produce samples bonded to Ti and fired at > 800 C in H_2 to produce both ohmic contacts and clean diamond surfaces with dangling bonds terminated with hydrogen. UPS, SEM, and photo emission studies are planned for the next reporting period.

We also plan to examine cost effective means to produce hole-electron pairs, such as N^+p electron injection from carbon implanted p type diamond. Carbon implanted diamond is reported to act like an N^+ semiconductor.

Testing Samples

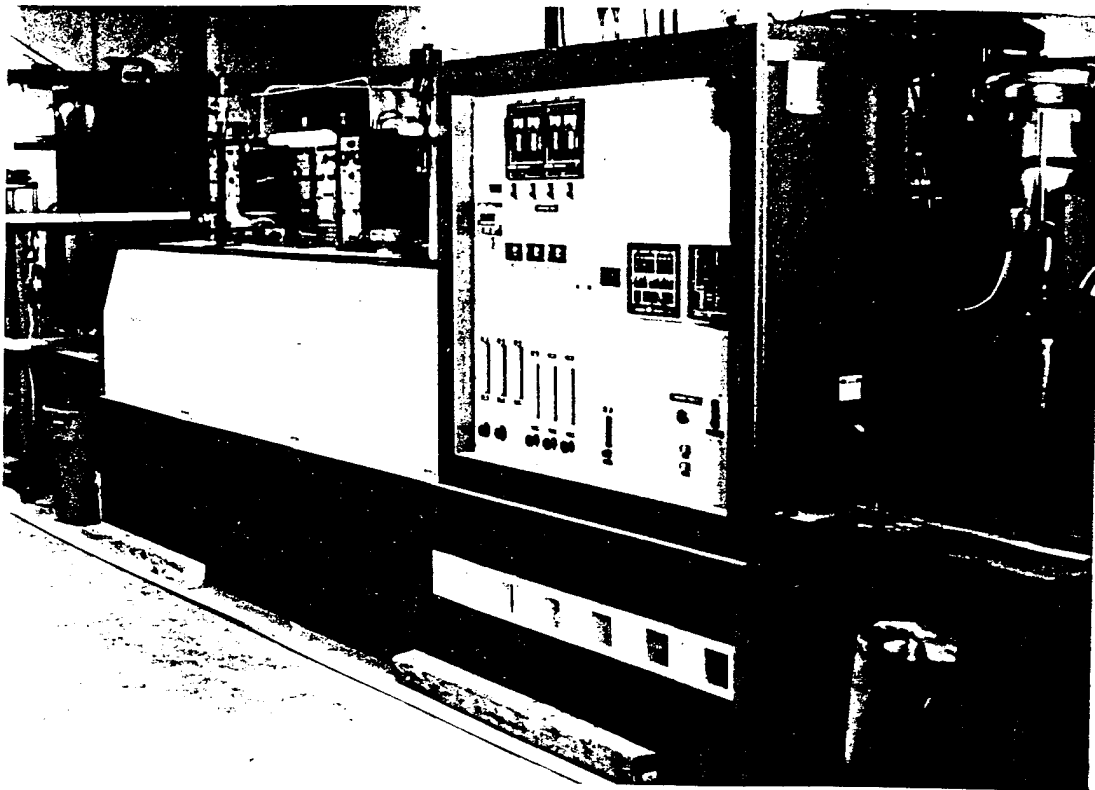
There are two areas in sample testing: emission testing and materials characterization. To test the electron emission of the samples, a vacuum chamber will be needed. Much work has been done in constructing and testing a chamber in coordination with related project(see photographs). The chamber must achieve a reasonable vacuum. The chamber is equipped with three pumps: a mechanical pump, a turbo pump, and an ion pump. Pressures on the order of 10^{-8} torr have been reached.

Next a source/measure unit (Keithly 237) was integrated into the system. This unit is capable sourcing voltage(or current) and measuring current(or voltage). Much work has been done in learning the software to run the source/measure unit as well as making sure the unit is operating correctly. The unit was tested with simple devices such as resistors and diodes at low currents(10^{-8} A). Low currents were tried to test the accuracy at small values. Also, some NEA materials were tested for emission within the chamber. The source/measure unit was brought into the chamber via feedthrough and connected to a vacuum cleaned point electrode. The sample is placed on a stage in the center of the six-way cross of the chamber. The electrode is mounted above the sample. A bias is applied across the sample with current being the measured parameter. Low emission currents(10^{-7} A) were obtained at 110 volts. The correctness of the results is being investigated.

The next stage is deciding on a light source and how to illuminate the sample within the chamber. Ultraviolet light of 222nm is needed to move electrons across the band gap of diamond(5.5eV). At present it appears a Xenon lamp with a MgF window on the chamber will be sufficient for our needs.

Testing the current density from the sample is the primary test for this project, but other evaluations are needed as well. John Driscoll has provided some samples of a copper/diamond paste on a silicon substrate. SEM photographs were obtained of these

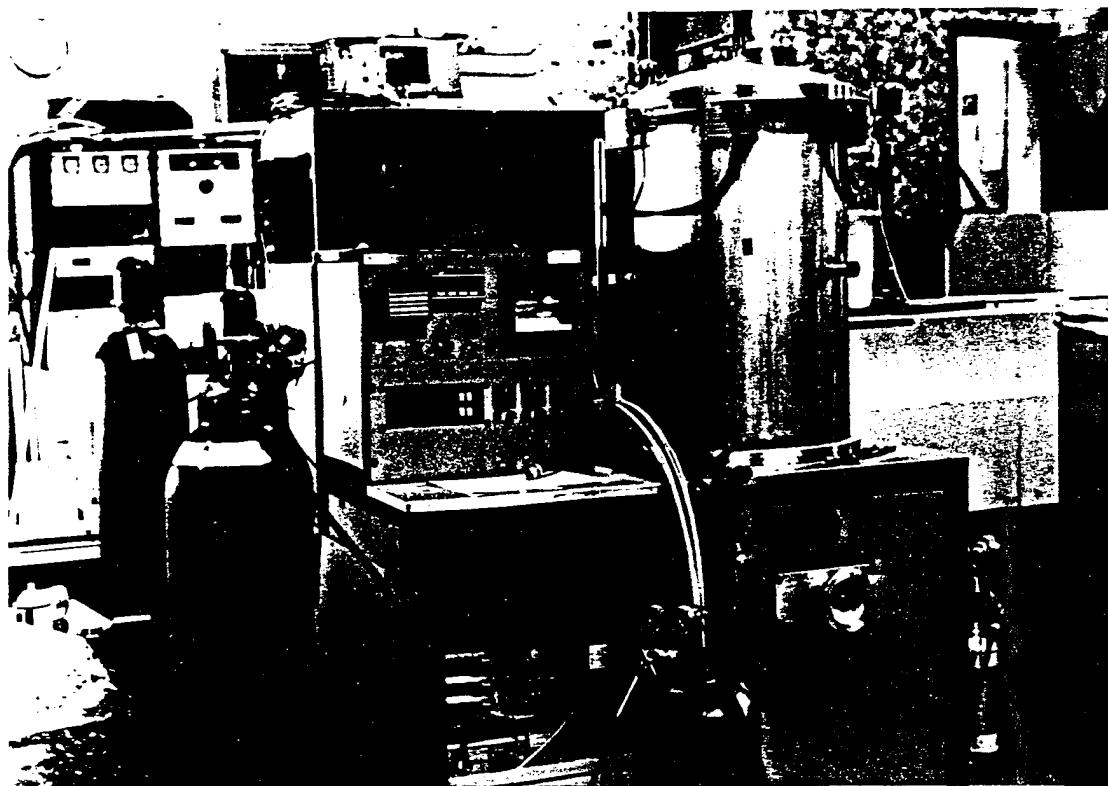
samples to indicate the surface morphology of the copper/diamond mix. Also, knowing whether the samples have NEA before testing current densities would be helpful. Thus, the samples from Driscoll are presently being examined with UPS(Ultra-violet photoelectron spectroscopy) to indicate if NEA exists. The vacuum level of NEA materials is below the conduction band. With UPS, electrons are excited to the conduction band by uv light. If the material has NEA the excited electrons in the conduction band have a probability of being emitted into the vacuum. Thus, UPS only qualitatively indicates NEA. Exposure to high temperatures can alter the composition of materials. Thus, samples are being analyzed by Raman spectroscopy to determine if diamond is present.



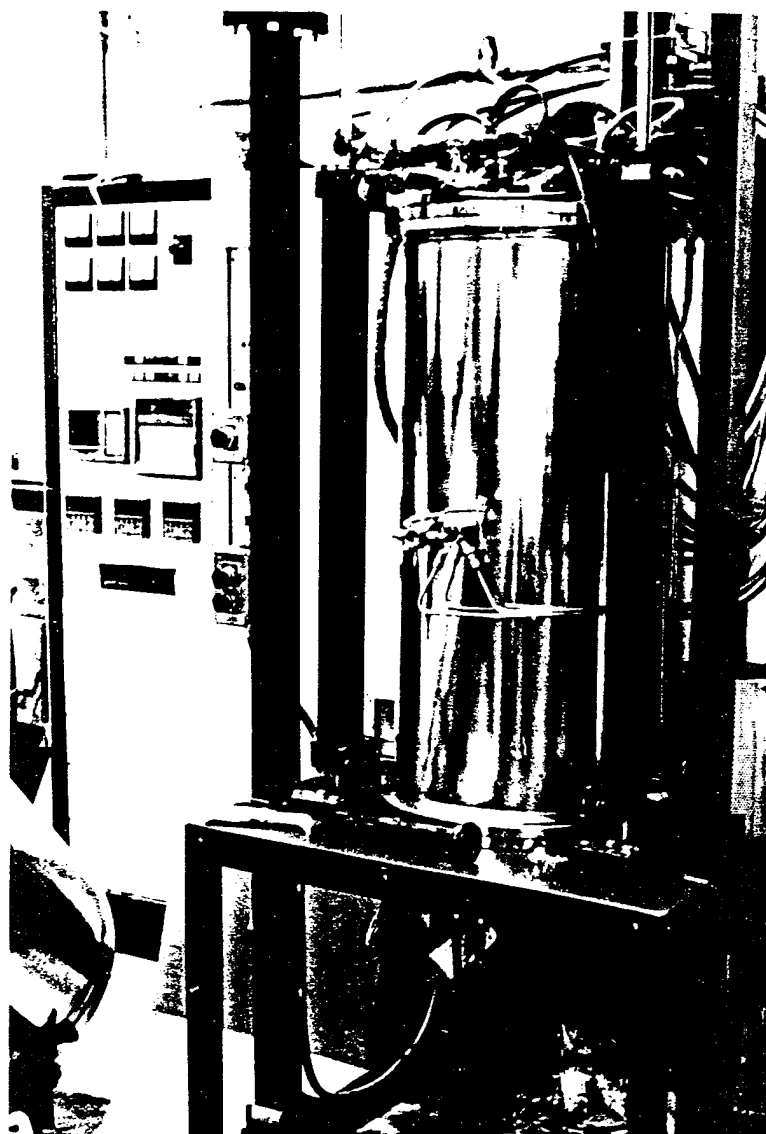
1. Four zone Thermco belt furnace



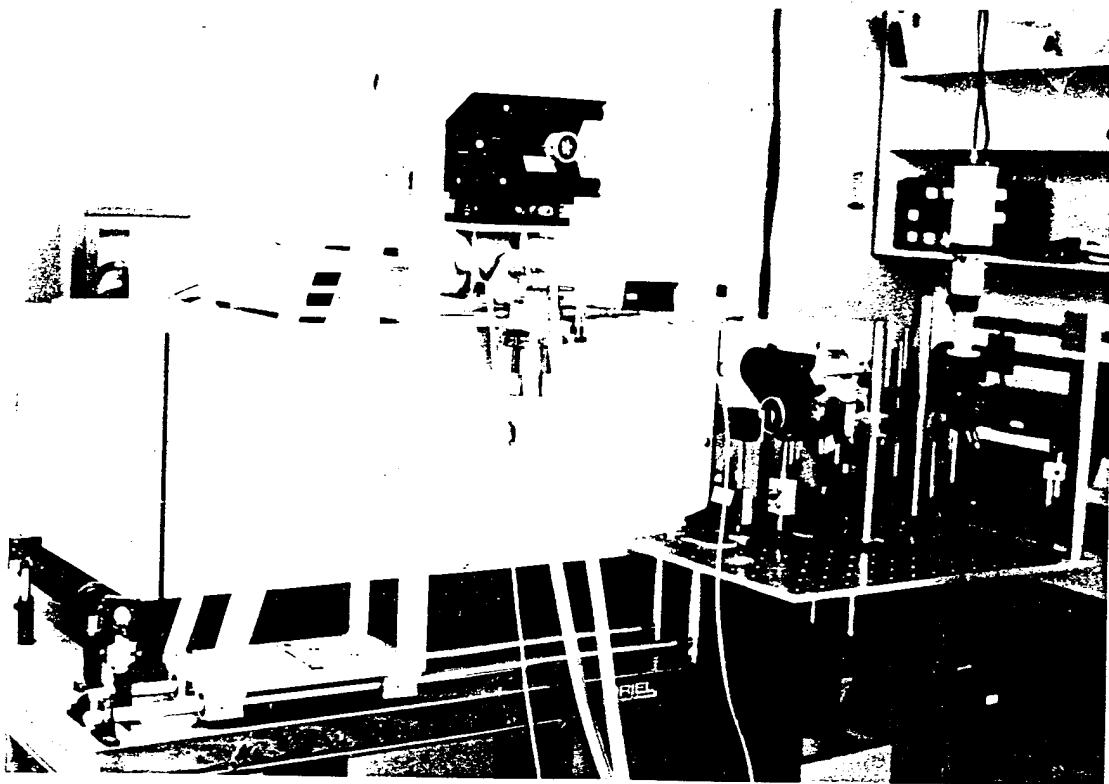
2. Pitt vacuum furnace, 1600° C, H_2/N_2



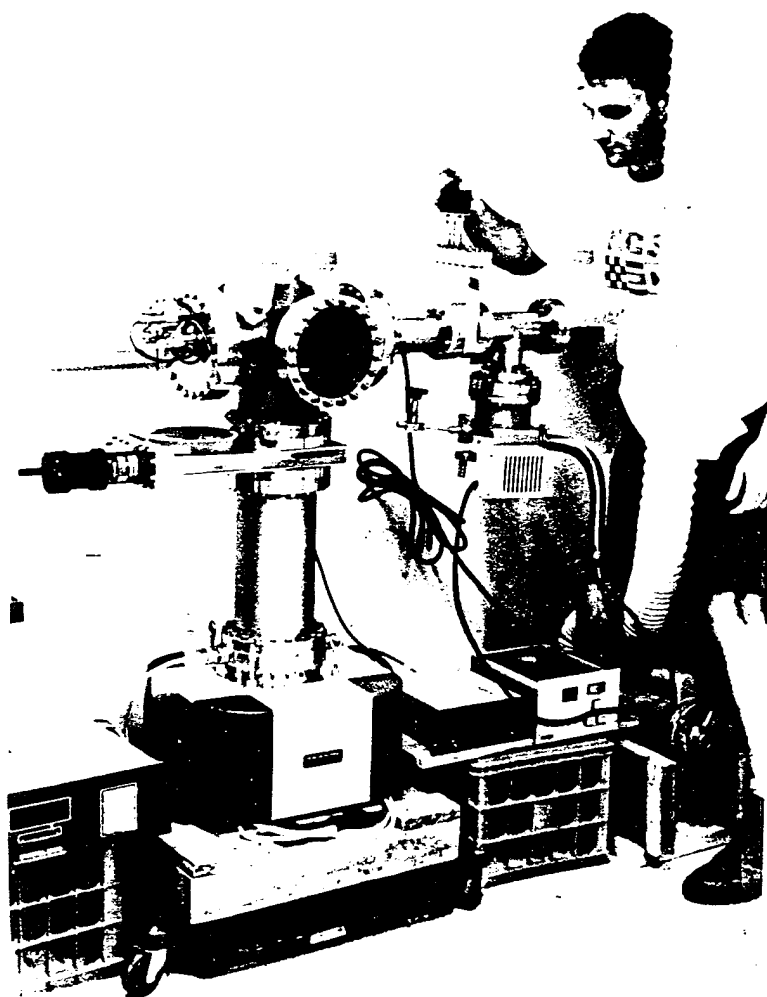
3. Camco vacuum furnace, 1200° C, Air



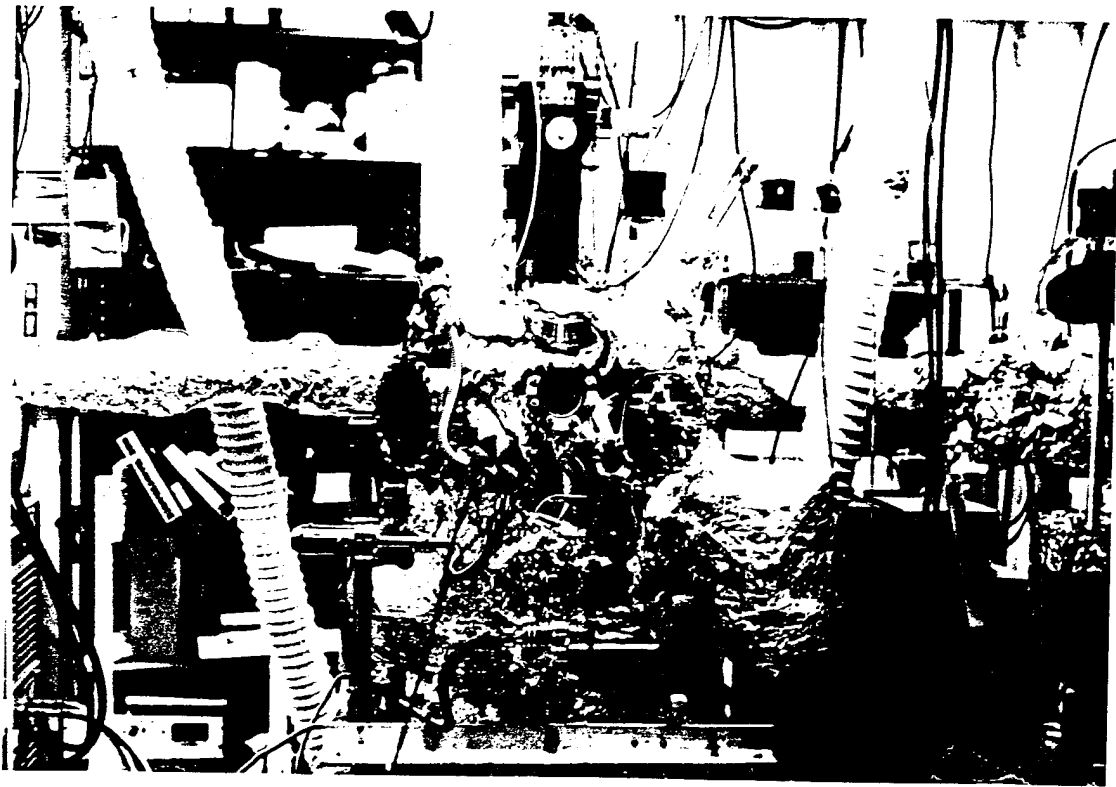
4. Astro vacuum furnace, 1600° C, H_2/N_2



5. Raman equipment at NCSU



6. High vacuum 6 cross emission test chamber



7. UPS (ultraviolet photo-emission spectrometer)

C-Cs (Carbon-Cesium)

Editor



Although there is no phase diagram available for the C-Cs system, the existence of C_xCs compounds ($x = 8, 24, 36, 48, 60$) [51Her, 59Hen, 59Rud] and $C_{10}Cs$ [61Sal] was reported in this system. The solubility of C in liquid Cs is $\log C \text{ (at. \%)} = -1.87 - 1240/T \text{ (K)}$ at 330 to 650 °C [86Bar]. The crystal structure data are from [Pearson3].—H.O.

51Her: A. Herold, *Compt. Rend.*, 232, 1484-1495 (1951) in French.

59Hen: G.R. Hennig, *Prog. Inorg. Chem.*,

C-Cs Crystal Structure Data

Phase	Composition, at.% Cs	Pearson symbol	Space group	Strukturbericht designation	Prototype
(C).....	0	<i>hP4</i>	<i>P63/mmc</i>	A9	C(graphite)
C_8Cs	11.1	<i>hP27</i>	<i>P6222</i>
(Cs).....	100	<i>cI2</i>	<i>Im3m</i>	A2	W

1, 125-205 (1959).
59Rud: W. Rudorff, *Adv. Inorg. Chem. Radiochem.*, 1, 223-266 (1959).
61Sal: J.F. Salzano and S. Aronson, *J. Inorg. Nucl. Chem.*, 26, 1456-1458

(1961).
86Bar: O.M. Barabash and Yu.N. Koval, *Crystal Structure of Metals and Alloys*, Naukova Dumka, Kiev, 196 (1986) in Russian.

C-Cu (Carbon-Copper)

P.R. Subramanian and D.E. Laughlin



The phase diagram for the Cu-C system is based on review of the experimental data [19Ruf, 46Bev, 69Mcl] and was obtained by thermodynamic modeling. The liquidus boundary has been drawn through the data of [46Bev] in the temperature range 1090 to 1797 °C, as well as through the data of [19Ruf] in the temperature range 2215 to 2300 °C. From the experimental data of [69Mcl], it is evident that the Cu-C phase diagram is of the peritectic type, with the peritectic horizontal lying at a temperature just above the melting point of Cu.

The equilibrium phases are (1) the liquid, L; (2) the fcc terminal solid solution (Cu), with about 0.04 at.% solubility of C; and (3) the graphite-type terminal solid solution (C), with no reported solubility of Cu.

Cu-C Crystal Structure Data

Phase	Composition, at.% C	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu).....	0 to 0.04	<i>cF4</i>	<i>Fm3m</i>	A1	Cu
(C).....	100	<i>hP4</i>	<i>P63/mmc</i>	A9	C(graphite)

[54Sne] reported the preparation of the compounds Cu_2C_2 and CuC_2 . The compounds were termed copper acetylides, because they resulted from the substitution of Cu for the hydrogen atoms of acetylene. Both Cu_2C_2 and CuC_2 were reported to be very unstable [54Sne].

19Ruf: O. Ruff and B. Bergdahl, *Z. Anorg. Allg. Chem.*, 106, 76-94 (1919) in German.

46Bev: M.B. Bever and C.F. Floe, *Trans. AIME*, 166, 128-141 (1946).

54Sne: M.C. Snead, J.L. Maynard, and R.C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. 2, Copper, Silver, and Gold, van Nostrand, Princeton, 110-111 (1954).

69Mcl: R.B. McLellan, *Scr. Metall.*, 3, 389-391 (1969).

Submitted to the APD Program. Complete evaluation contains 2 figures, 3 tables, and 12 references.

8. Cu-C phase diagram a and b.

C-Dy (Carbon-Dysprosium)

K.A. Gschneidner, Jr. and F.W. Calderwood



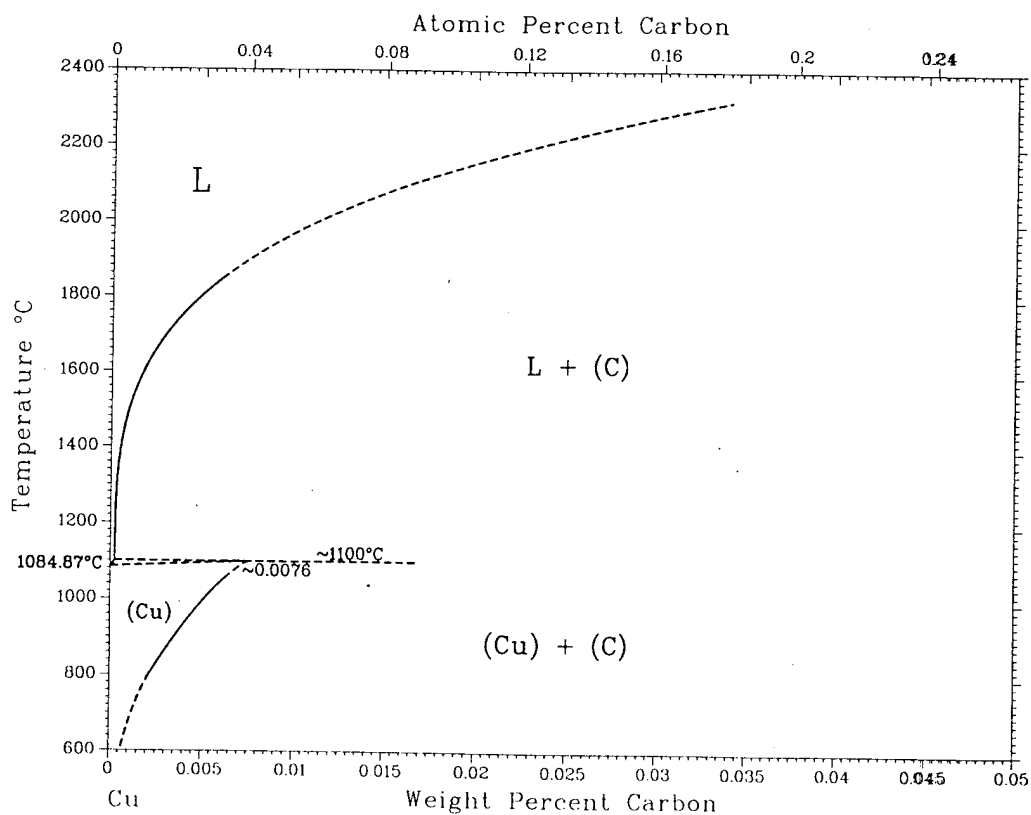
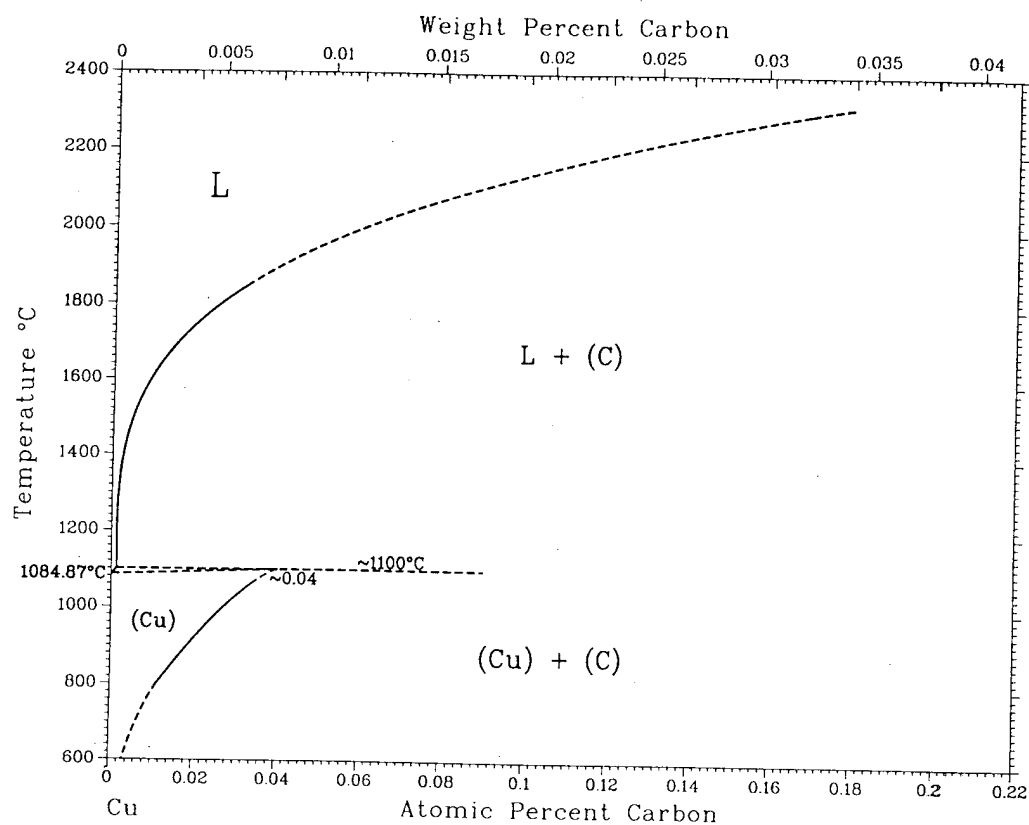
No phase diagram is available for the Dy-C system, but some structural data have been re-

ported. [58Spe] found that compositions near Dy_3C form a NaCl defect structure (i.e., the Fe_4N -type struc-

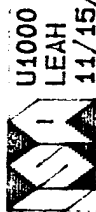
ture). The Fe_4N -type phase is the high-temperature form, which can exist at room temperature in a metastable



Cu-C Phase Diagram



P.R. Subramanian and D.E. Laughlin, submitted to the APD Program.



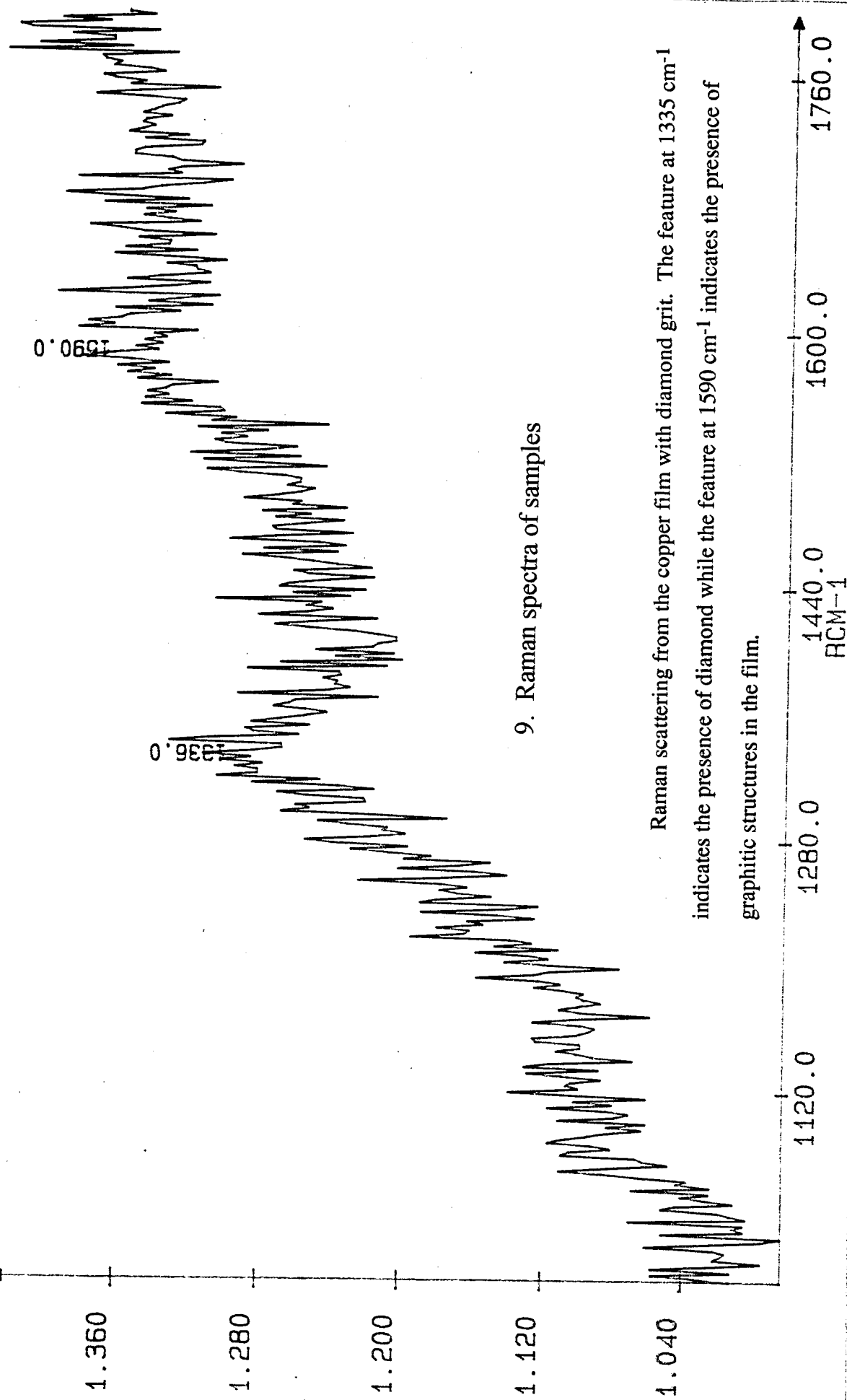
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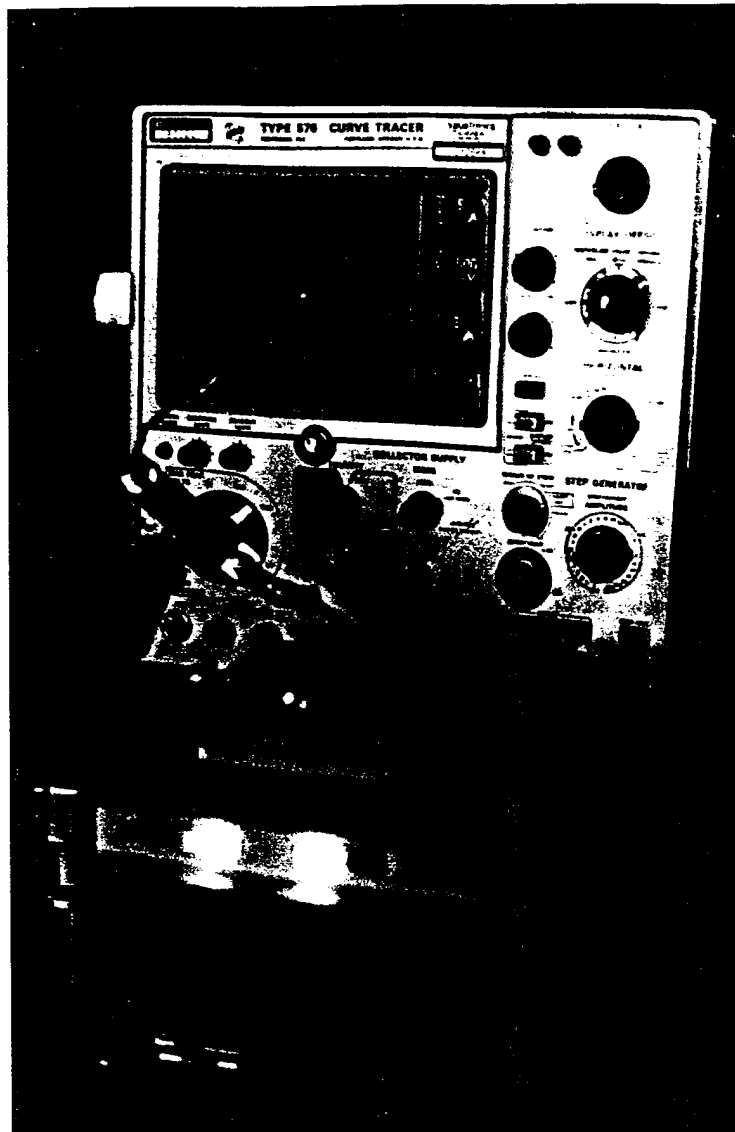


9. Raman spectra of samples

Raman scattering from the copper film with diamond grit. The feature at 1335 cm^{-1} indicates the presence of diamond while the feature at 1590 cm^{-1} indicates the presence of graphitic structures in the film.



10. Gem photos of samples



11. Tektronix 576 curve tracer